Effects of Fe Substitution on the Electronic Structure of $YBa_2Cu_3O_y$ Investigated by NEXAFS

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Introduction: Partial substitution of Cu by Fe in the high-temperature superconductor $YBa_2Cu_3O_y$ strongly suppresses T_c; annealing at high oxygen pressure is able to restore T_c to a certain degree [1]. Fe mainly substitutes on the Cu(1) chain sites; unlike Cu it prefers a tetrahedral or pyramidal oxygen coordination [1,2] which in turn leads to the formation of zigzag chains and to an orthorhombic-tetragonal transition [2]. Often y is seen to increase with Fe content, although y and T_c as well as the fraction of the doped Fe atoms going to the planar or to the chain sites all heavily depend on preparation conditions. Structural, magnetic, and superconducting properties of $YBa_2Cu_{3-x}Fe_xO_y$ are well studied, and yet – despite some earlier efforts by NEXAFS, Mößbauer, and Raman experiments – a detailed investigation of the *electronic* structure has sorely been missing.

Methods and Materials: We characterized a series of $YBa_2Cu_{3-x}Fe_xO_y$ single crystals for various values of Fe content x and O content y by EDX, neutron and x-ray diffraction (showing that y indeed increases slightly with x and that y is higher for samples annealed at high oxygen pressure) and investigated their unoccupied electronic structure by polarization-dependent NEXAFS in bulk-sensitive fluorescence yield mode at the O 1*s*, Cu 2*p*, and Fe 2*p* absorption edges.

Results: O 1*s* and Cu 2*p* NEXAFS indicates that with increasing x the total number of hole states is reduced, and that this occurs with different rates for different sites: the effect is largest for the chain O(1) sites and smaller for the planar O(2,3) sites, while the spectral weight associated with the apical O(4) sites even remains constant and is just redistributed slightly in energy. Annealing at high oxygen pressure restores the depleted spectral weight, consistent with the higher oxygen content. The total hole count turns out to depend linearly on x for both high-pressure and ambient pressure oxygen annealing, and the average Fe valence (calculated from x, y, and the total hole count) is mostly consistent with Fe^{3+}. Comparing the Fe 2*p* spectra to calculated branching ratios [3] allows to identify different spin states for Fe in different compounds; the results show that Fe goes almost exclusively to chain sites (thus effectively excluding magnetic pair breaking as a possible cause for T_c suppression) and that a spin transition takes place upon reducing the oxygen content.

Conclusions: The results show that charge carrier depletion is the main cause for T_c suppression in $YBa_2Cu_{3-x}Fe_xO_y$. While an additional effect from disorder cannot be excluded magnetic pair breaking does not play a role at all.

References: [1] F. Shi, R. Harris, W.J. Bresser, D. McDaniel, and P. Boolchand, J. Phys.: Cond. Matt. **9**, L307 (1997); [2] F. Bridges, J.B. Boyce, T. Claeson, T.H. Geballe, and J.M. Tarascon, Phys. Rev. B **39**, 11603 (1989); H. Renevier, J.L. Hodeau, M. Merzio, and A. Santoro, Physica C **220**, 143 (1994); S.V. Zheludkov and A.T. Maylibaev, Phys. Lett. A **159**, 417 (1991); C.P. Burmester, L.T. Wille, and R. Gronsky, Solid State Commun. **77**, 693 (1991); [3] B.T. Thole and G. van der Laan, Phys. Rev. B **38**, 3158 (1988).